Effect of chemical treatment on the pyrolysis of waste bagasse

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学　位　論　文　題　目　**Effects of chemical treatment on the pyrolysis of waste bagasse (熱分解によるバガスの化学原燃料転換に及ぼす化学的処理の効果)**
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論　文　内　容　要　旨

[Introduction] With the increasing environmental problems associated with solid wastes, comprehensive solid waste management should be exercised. In Fiji, the main method for waste treatment is landfilling, which has numerous environmental problems including leaching of toxic matter into the seas. The sugar industry has been perceived as the backbone of Fiji's economy since the 1970's, with 70% of export earnings[1].

Bagasse is the lignocellulosic dry material after the juices have been squeezed out of sugarcane. Currently, it is used for production of steam for the mill processes via direct combustion. However, about 40% of the bagasse production remains after every crushing season[2] and they are good feedstock for chemical conversion. Plastic wastes are also increasing in Fiji. Unfortunately, there is no efficient technology currently in place in Fiji to recycle the plastic generated wastes.

Therefore, this research is suggests possible recycling of bagasse via pyrolysis. The pyrolysis of biomass is challenging due to their tight network of lignocellulosic structure, cellulose, hemicellulose and lignin[3], hence chemical treated with acid was done, and also the co-pyrolysis with waste plastics. Acid pretreatment was selected for this work since it can shorten the cellulose chains making them easier to pyrolyze.

The main objective of this research is to provide a method for the recycling of waste bagasse, at the same time providing renewable energy and chemical sources via pyrolysis.

[Acid pretreatment of sugarcane bagasse] Bagasse obtained from Fiji Sugar Corporation was dried at 105℃ for 48 h, grounded and sieved to a particle fraction below 125 μm. Ultimate,

proximate and compositional analysis was carried out on the samples. Solutions (100 mL) of 1, 3, 6 and 9 M acetic acid concentrations were prepared, and 1 g of bagasse samples was added to the solution

Table 1 Proximate, ultimate, and component analysis of untreated and acid pretreated bagasse

	Ultimate analysis (wt%)					Component Analysis (wt%)				
	C	H	O[*1]	N	S	Cell	Hemi	Lig[*1]	Extrac	Ash
Untreated	42.7	6.1	50.7	0.5	+[*2]	30.9	28.2	9.6	11.4	12.8
1 M CH_3COOH	44.5	5.9	49.0	0.6	0.1	42.3	22.9	10.6	14.2	15.4
3 M CH_3COOH	43.6	5.5	50.2	0.6	0.1	41.5	23.6	13.8	9.2	11.4
6 M CH_3COOH	43.9	5.6	49.7	0.7	0.1	39.2	21.2	14.4	9.8	11.3
9 M CH_3COOH	37.5	5.0	57.0	0.5	+	40.9	20.9	14.5	13.8	11.7

[*1] calculated by weight difference; [*2] value less than 0.05

Weight loss increased with increasing acid concentration, from 13.4 to 25.8 wt% for 1 and 9 M CH_3COOH respectively. This is attributed to the hydrolysis of polysaccharides, mainly hemicellulose, which reduced slightly after pretreatment (Table 1). The ratio of cellulose increased in the sample after acid pretreatment. TG/ DTG curves (Fig. 1) had the shift of cellulose peaks to lower temperatures and lowering of hemicellulose peaks with increasing acid concentrations. This proves the shortening of these chains by acid pretreatment, making them degrade at lower temperatures. FT-IR analysis O-H vibrations also did not alter much with acid pretreatment, which suggests even after hydrolysis has occurred; the structural make-up of the bagasse did not change much.

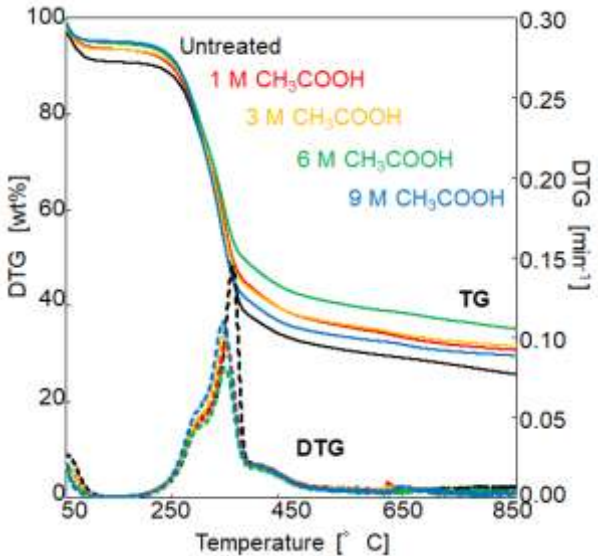

Fig. 1 TG/DTG of untreated and acid pretreated bagasse

[Pyrolysis of acid pretreated bagasse] Pyrolysis was performed in a quartz tube reactor heated by an electric furnace. The set-up has been published elsewhere [5]. There were 4 conditions investigated, namely (1) pyrolysis at 500 °C, (2) temperature increased to 800 °C, (3) addition of steam to second reaction chamber and (4) wet bagasse. Acid pretreated improved the pyrolysis of bagasse (Fig. 3). The gaseous yield increased from 18.7 to 22.2 wt% for untreated and 1 M CH_3COOH pretreatment, respectively. The shortening of cellulose and

hemicellulose chain after acid pretreatment improved the pyrolysis of sugarcane bagasse. The amount of CO and CO_2 reduced with increasing acid concentration (Fig. 2) due to the hydrolysis reaction, which CH_4 ratios increased due to the high lignin fractions after acid pretreatment.

Temperature increase to 800 °C increased the gaseous products from 22.2 to 45.1 wt% for 1 M CH_3COOH pretreated bagasse at 500 and 800 °C. This increase in gaseous yield is associated with the reduction in tars. This suggests that thermal cracking of tars to give high gaseous yields.

The addition of steam was seen to increase the gaseous yield even further. This is attributed to waster-gas shift reactions which would have taken place at such high temperatures. Also, the yield of H_2 gases was enhanced.

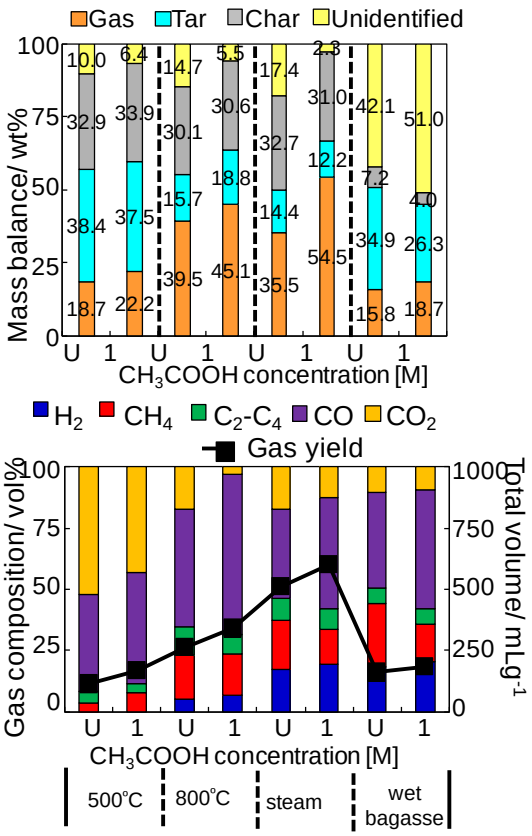

Fig. 2 Mass balance and gaseous products of the pyrolysis of untreated and 1 M CH_3COOH bagasse under different conditions

[Co-pyrolysis-gasification of bagasse and waste plastics] A mixture of mixed plastics (MP) including polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) were ground and sieved to obtain particles sizes between 100 and 125 µm, and mixed (PE:PP:PS:PET:PVC, 32.6:22.8:21.6:16.9:6.1) according to the realistic waste plastic composition in Japan [4]. The co-pyrolysis-gasification of bagasse and waste plastics was done in a bagasse:plastic ratio of 1:1

The co-pyrolysis of acid pretreated bagasse and waste plastics was seen to increase the gaseous yield even further, under each condition (Fig. 3). Also, the H_2 production was enhanced, due to the contribution by the H-rich plastic wastes. The C_2-C_4 components of the bagasse were also enhanced, due to the polyethylene contribution present in the plastic wastes. In an aim to increase the gaseous yield, and H_2 production, the co-pyrolysis of bagasse and waste plastics

was carried out using a Ni catalyst. This saw the further increase in gaseous yields and also the production of H_2 (Fig. 3). The a ddition of waste plastics into the co-pyrolysis-gasification reaction not only has technical advantages in the selection of H_2 and other products, it also contributes to the management of wastes in Fiji

[Conclusion] The conversion of bagasse into gases, tars ad char was successfully carried out in this work. The yields were enhanced by acid pretreatment, and also via co-pyrolysis with waste plastics. This pyrolysis technique offers a suitable solution for treating waste bagasse and plastics in Fiji. The technology can be introduced to any other biomass wastes in Fiji, as pyrolysis can treat a wide variety of waste feedstock.

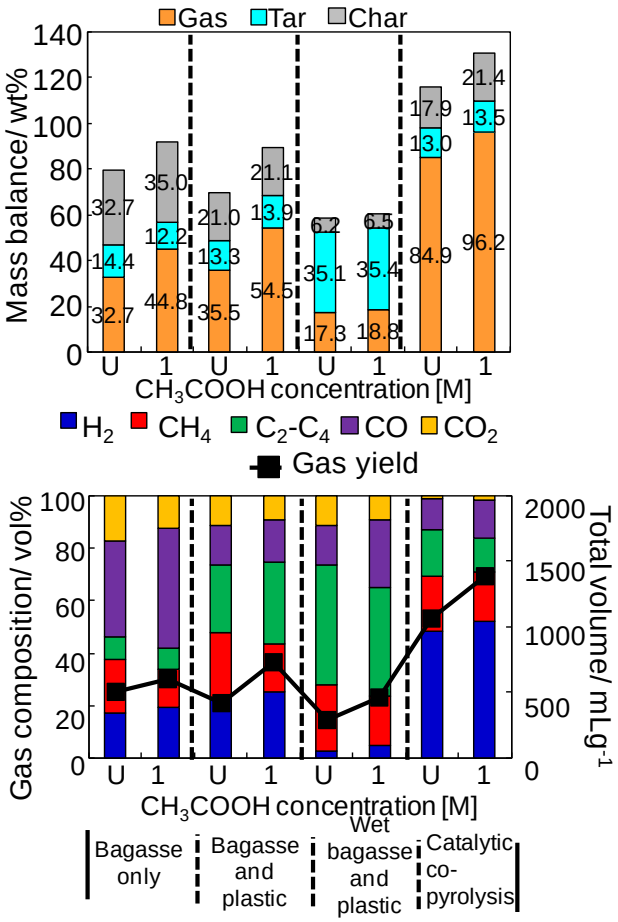

Fig. 3 Mass balance of the co-pyrolysis of untreated and 1 M CH_3COOH bagasse and waste plastics under different conditions

Reference [1] Narayan, P. K.et al. *Fijian Studies: A Journal of Contemporary Fiji* **2003,** *1* (1), 3. [2] Prasad, S., *Fijian Studies: A Journal of Contemporary Fiji* **2003,** *1* (2), 243. [3] Fan, L.et al. In *Microbial reactions,* Springer: 1982; pp 157-187. [4] Honus, S. et al. *Energy Conversion and Management* **2016,** *126*, 1118-1127. [5] Kumagai, S.et al. *Journal of Analytical and Applied Pyrolysis* **2015,** *113*, 15-21.

（別紙）

論文審査結果の要旨及びその担当者

論文提出者氏名	Viliame Savou
論　文　題　目	熱分解によるバガスの化学原燃料転換に及ぼす化学的処理の効果 Effect of chemical treatment on the pyrolysis of waste bagasse
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論文審査結果の要旨

フィジーにおいて砂糖産業は経済を支える重要な産業であり、その原料となるサトウキビの生産量は年間 180 万トンに達する。したがって砂糖の製造工程で発生する搾りかす（バガス）は大量であり、バガスの有効利用技術の開発はフィジーにおける喫緊の課題となっている。一方、フィジーではプラスチック需要が年々増加しており、廃プラスチックの適正処理およびリサイクルの早期実現が重要である。本論文は、このような背景から、バガスおよびプラスチックを同時に処理可能な手法として熱分解法に着目し、熱分解法による化学原燃料転換の効果向上を目的に、バガスに対する種々の化学的処理の影響を検討した。

第１章は緒論であり、上述のような研究の背景および目的を述べた。

第２章は、バガスの主要構成成分であるセルロース、ヘミセルロース、およびリグニンを低分子量化することを目的に、各種無機酸および有機酸によるバガス処理の効果を検討した。酸処理によりこれら成分のエーテル結合が開裂し、成分構成比が大きく変化することなく低分子量化され、かつ脱灰されることが明らかとなった。

第３章は、第２章において調製した各種酸処理バガスを熱分解し、熱分解生成物組成に及ぼす酸処理の影響を調査した。その結果、酸処理したバガスの液体生成物の収率は未処理のバガスに比べて向上することを明らかにした。さらに、水蒸気添加により水素収率が向上すること、湿った状態の酸処理バガスの熱分解においては炭化物が大きく減少することも明らかとなった。

第４章では、第２章および第３章においてバガス酸処理の効果が認められたため、さらに、廃プラスチック（PE:33%, PP:23%, PS:21%, PVC:6% PET:17%）を添加した共熱分解を実施した。プラスチックとバガスをそれぞれ熱分解するよりも、共熱分解によってガス収率が向上するシナジー効果が発現することを見出した。さらに、共熱分解生成物をアルミナ担持ニッケル触媒により水蒸気改質することでガス化が促進され、水素リッチなガス回収が可能であることも確認した。

第５章は本研究の総括であり、得られた成果のまとめ、本研究の社会的および学術的意義について述べた。

以上、本論文で明らかにした熱分解によるバガスの化学原燃料転換に及ぼす化学的処理の効果は、今後、フィジー始め砂糖産業が盛んな地域におけるバガスの有効利用技術の開発に向けた重要知見となると同時に、関連する学問分野の発展にも寄与することが大きく期待される。

よって、本論文は博士(環境科学)の学位論文として合格と認める。